GROWTH OF *IN-SITU* THIN FILMS BY REACTIVE EVAPORATION

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FIELD OF THE INVENTION

[0002] The field of the invention generally relates methods used

15 to produce thin films. More specifically, the field of the invention relates to methods of forming films *in-situ* such as superconducting MgB_2 that do not require high temperature annealing.

BACKGROUND OF THE INVENTION

20 [0003] Magnesium diboride (MgB_2) is a superconducting material having a superconducting transition temperature (T_c) of approximately 39 K. There is a significant interest in using MgB_2 to form superconducting wires, tapes, and films. Superconducting wire, for example, can be used for

25 superconducting magnets, fault-current limiters, and power transmission. Films can be used to make Josephson junctions, SQUIDS (superconducting quantum interference devices), micro-

1

electronic interconnects, RSFQ (rapid single flux quantum) devices, and other devices. Films can also be incorporated into RF and microwave devices in the form of resonators, filters, delay lines, and the like.

5 [0004] With respect to film applications, growth of completely *in-situ* MgB$_2$ films is required in order to realize the multilayer technology necessary for electronics applications. The primary difficulty of depositing MgB$_2$ films is the very high vapor pressures of Mg required for the thermodynamic stability of the

10 MgB$_2$ phase at elevated temperatures. A second problem relating to MgB$_2$ film formation is the high sensitivity of Mg to oxidation. Both of these concerns have made it difficult to grow MgB$_2$ films using conventional physical vapor deposition (PVD) techniques.

15 [0005] *In-situ* MgB$_2$ films have been fabricated by annealing Mg-B or Mg-MgB$_2$ mixtures *in situ* in growth chambers. However, films produced by such techniques have shown a lower T$_c$ and poor crystallinity. *In-situ* MgB$_2$ films have also been fabricated at low temperatures (<350°C) but these films are not epitaxial,

20 their crystallinity is poor, their T$_c$ values are low, and their resistivities are high. Zeng et al. have grown MgB$_2$ films *in-situ* by using HPCVD (hybrid physical-chemical vapor deposition) techniques. *See* X.H. Zeng et al., *In situ epitaxial MgB$_2$ thin films for superconducting electronics*, Nature Materials 1, pp.

1-4 (2002). However, this method is not readily amenable to multilayer devices or applications requiring large-area film growth. Furthermore, the substrate temperature used in the method proposed by Zeng et al. is above 700°C, and growth has

5 been successful only on a limited number of substrate materials.

[0006] There thus is a need for a method of producing MgB$_2$ films *in-situ* within a temperature range of approximately 300°C to approximately 700°C. A method is also needed that can grow MgB$_2$ films *in-situ* on a variety of substrate materials. A method is

10 needed that can produce *in-situ* MgB$_2$ suitable for use in multilayer device fabrication. The method is also preferably applicable to superconducting films other than MgB$_2$.

SUMMARY OF THE INVENTION

15 [0007] In a first aspect of the invention, a method of forming MgB$_2$ films *in-situ* on a substrate comprises the steps of (a) depositing boron onto a surface of the substrate in a deposition zone; (b) moving the substrate into a reaction zone containing pressurized, gaseous magnesium; (c) moving the substrate back

20 into the deposition zone; and (d) repeating steps (a)-(c).

[0008] In a second aspect of the invention, a MgB$_2$ film is created using the method of the first aspect.

[0009] In a third aspect of the invention, a method of forming a thin film of MgB$_2$ *in-situ* comprises the steps of providing a

rotatable platen, the platen being rotatable within a housing having a reaction zone and a separate deposition zone, providing an evaporation cell coupled to the reaction zone, the evaporation cell containing magnesium. A source of boron is

5 provided adjacent to the deposition zone and an electron beam is aimed at the source of boron. The substrate is loaded onto the platen and the platen is then rotated. The local environment around the substrate is heated. The evaporation cell is heated to produce gaseous magnesium in the reaction zone. Boron is

10 evaporated using the electron beam gun.

[0010] In a fourth aspect of the invention, a MgB$_2$ film is created using the method of the third aspect.

[0011] In a fifth aspect of the invention, a method of forming a superconducting film of a known superconducting compound *in-situ*

15 on a substrate comprising the steps:(a) depositing one or more elements of the superconductor onto a surface of the substrate in a deposition zone;(b) heating a non-gaseous element of the superconductor so as to produce a pressurized gaseous phase of the element inside a reaction zone;(c) moving the substrate into

20 the reaction zone containing the pressurized gaseous element; (d) moving the substrate back into the deposition zone; and (e) repeating steps (a)-(d).

[0012] It is an object of the invention to provide a method for making MgB$_2$ films *in-situ* on a substrate.

[0013] It is a further object of the invention to provide a method for making MgB_2 film *in-situ* on a substrate in which the substrate is heated to a temperature within the range of about 300°C to about 700°C.

[0014] It is a further object of the invention to provide a method for making MgB_2 films *in-situ* on multiple sides of a substrate.

[0015] It is another object of the invention to provide a method for making films *in-situ* of known superconductor.

[0016] These and further objects of the invention are described in more detail below.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] Fig. 1 illustrates a preferred device used to form a film of MgB_2 *in-situ*.

[0018] Fig. 2 illustrates a perspective view of the underside of the pocket heater shown in Fig. 1.

[0019] Fig. 3 is a flow chart of a preferred process of making a film of MgB_2 *in-situ*.

[0020] Fig. 4 is a flow chart of another preferred process of making a film of MgB_2 *in-situ*.

[0021] Fig. 5 illustrates the resistivity of a MgB_2 film deposited on a polycrystalline alumina substrate.

[0022] Fig. 6 illustrates the resistance of a MgB_2 film deposited on flexible stainless steel tape.

[0023] Fig. 7 illustrates the resistivity of a MgB_2 film deposited on LSAT.

[0024] Fig. 8 illustrates the resistivity of a MgB_2 film deposited on $LaAlO_3$.

5   [0025] Fig. 9 illustrates the resistivity of a MgB_2 film deposited on MgO.

[0026] Fig. 10 illustrates the resistivity of a MgB_2 film deposited on $SrTiO_3$.

[0027] Fig. 11 illustrates the resistivity of a MgB_2 film deposited

10   on YSZ.

[0028] Fig. 12 illustrates the resistivity of a MgB_2 film deposited on r-plane sapphire.

[0029] Fig. 13 illustrates the resistivity of a MgB_2 film deposited on c-plane sapphire.

15   [0030] Fig. 14 illustrates the resistivity of a MgB_2 film deposited on m-plane sapphire.

[0031] Fig. 15 illustrates the resistivity of a MgB_2 film deposited on 4H-SiC.

[0032] Fig. 16 illustrates the resistivity of a MgB_2 film deposited

20   on Si_3N_4/Si.

[0033] Fig. 17 is a plot of estimated surface resistance values of MgB_2 film deposited on sapphire and alumina substrates.

[0034] Fig. 18 illustrates a device according to one preferred

aspect of the invention for depositing thin films on a long

ribbon of tape.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

5   [0035] Fig. 1 illustrates a preferred device 2 used to fabricate

in-situ MgB_2 films. The device 2 includes a vacuum chamber 4

having a removable or openable lid 6 that permits a user to gain

access to the interior of the vacuum chamber 4. The vacuum

chamber 4 is connected via a vacuum hose 8 to a vacuum pump 10.

10   During operation, the pressure inside the vacuum chamber 4 is a

high vacuum -- preferably less than 10^{-6} Torr.

[0036] A pocket heater 12 is provided inside the vacuum chamber 4

and is used to repeatedly move one or more substrates 14 between

a deposition zone 16 in which boron is deposited on the one or

15   more substrates 14 and a reaction zone 18 in which pressurized,

gaseous magnesium reacts with the deposited boron to form an *in-

situ* MgB_2 film. The pocket heater 12 includes a housing 20 which

partially encloses the substrates 14 as described in more detail

below. The housing 20 preferably includes heating coils (not

20   shown) for heating substrates 14 contained within the interior

of the pocket heater 12. Preferably, there is a top heating

coil, a side heating coil, and a bottom heating coil although

other constructions may be used. The heating coils can heat the

pocket heater 12 to a temperature exceeding 800°C, although growth temperatures between 300°C and 700°C are preferred.

[0037] The housing 20 of the pocket heater 12 includes an upper portion 22 which completely covers an upper surface of the

5   substrates 14. The housing 20 also includes a lower portion 24 which partially encloses the underside surface of the substrates 14. As best seen in Fig. 2, a pie-shaped wedge is removed from the lower portion 24 of the housing 20 to form the deposition zone 16. The lower portion 24 of the housing 20 that does

10 enclose the substrates 14 forms a reaction chamber 26 (i.e., reaction zone 18) between the underside of the substrates 14 and the interior surface of the lower portion 24 of the housing 20. The reaction chamber 26 is disposed close enough to the underside of the substrates 14 such that a localized high

15 pressure region of magnesium gas is created in the reaction chamber 26. While this pressure has not been measured, it has been reported by others that at 750°C, the required vapor pressure of magnesium is about 10 mTorr in the thermodynamic growth window. It should be understood that "high pressure" in

20 the context of the reaction chamber 26 is a relative term and the pressure within the reaction chamber 26 is above the pressure in the vacuum chamber 4 but significantly less than atmospheric pressure.

[0038] A gap 28 is formed between the underside of the substrates 14 and the lower portion 24 of the housing 20. Preferably, the size of this gap 28 can be adjusted by moving the lower portion 24 of the housing 20 towards or away from the substrates 14.

5   Preferably, the gap 28 formed has a width within the range of about 0.005 inch to about 0.015 inch.

[0039] A rotatable platen 30 is disposed inside the housing 20 of the pocket heater 12 and is used to rotatably support one or more substrates 14. Fig. 2 illustrates a substrate 14 being

10   held by the platen 30 in the deposition zone 16. The substrate 14 held by the platen 30 may take any number of shapes and forms, including but not limited to, a wafer, chip, flexible tape, or the like. The present method has been used to deposit MgB_2 films onto up to three 2" wafers at once, or a single 4"

15   wafer. In addition, the present method of fabricating *in-situ* MgB_2 films can be used with a wide variety of substrate 14 materials. These include by way of illustration and not limitation: LSAT, $LaAlO_3$, MgO, $SrTiO_3$, r-plane sapphire, c-plane sapphire, m-plane sapphire, yttria-stabilized zirconia (YSZ),

20   silicon carbide, polycrystalline alumina, silicon, and stainless steel. With respect to silicon, a Si_3N_4 buffer layer is first formed on the silicon substrate. It is believed that the present method can be used to deposit MgB_2 films on any substrate

in which there is no chemical reaction with magnesium, boron, or MgB_2.

[0040] Consequently, the present method provides a novel way of forming MgB_2 films on a variety of technologically interesting

5   and inexpensive substrates. Coated conductor applications are thus possible. In addition, MgB_2 films can be deposited on flexible tapes.

[0041] Still referring to Fig. 1, the rotatable platen 30 is mounted on a rotatable shaft 32 that passes through the housing

10   20 of the pocket heater 12. The rotatable shaft 32 is mechanically connected at one end to a motor or servo (not shown) that drives the shaft 32 and thus rotates the platen 30. Preferably, the platen 30 is removable from the shaft 32 such that loading and unloading of the substrates 14 from the platen

15   30 can take place outside of the pocket heater 12 and vacuum chamber 4.

[0042] A magnesium evaporation cell 34 is provided inside the vacuum chamber 4. The magnesium evaporation cell 34 contains heater coils 36 which are used to heat solid magnesium 38

20   contained within the evaporation cell 34. The magnesium evaporation cell 34 is heated to a temperature of at least 550°C and more preferably around 650°C so as to create magnesium vapor. This temperature can be adjusted to control the pressure of gaseous magnesium within the reaction chamber 26. A

magnesium feed tube 40 connects the magnesium evaporation cell

34 to the reaction chamber 26 of the pocket heater 12. The

magnesium feed tube 40 is preferably heated by heater coils 42

so that magnesium does not condense on the inside of the feed

5   tube 40. Preferably, about 9 amps of power is supplied to the

heater coils 42 so as to maintain the magnesium feed tube 40 at

a higher temperature than the magnesium evaporation cell 34. Of

course a higher or lower amount of power may be used depending

on the particular heating coils 42 used.

10   [0043] As an alternative to the magnesium evaporation cell 34 and

feed tube 40, a source of magnesium can simply be placed inside

the reaction chamber 26 of the pocket heater 12 wherein it will

evaporate to form a high pressure gas inside the magnesium

reaction chamber 26.

15   [0044] Still referring to Fig. 1, an electron beam crucible 44 is

disposed inside the vacuum chamber 4 and beneath the deposition

zone 16. Boron 46 is placed inside the electron beam crucible

44. An electron beam gun 48 is positioned inside the vacuum

chamber 4 and is aimed at the electron beam crucible 44

20   containing the boron 46. The electron beam gun 48 is used to

heat the boron 46 to a sufficiently high enough temperature such

that the boron 46 starts to evaporate.

[0045] While the use of an electron beam gun 48 is preferred, the boron 46 may be deposited by any other method known to those skilled in the art.

[0046] Two quartz crystal monitors (QCM) 50, 52 are optionally

5   included in the vacuum chamber 4. A first QCM monitor 50 is preferably aimed downward toward the electron beam crucible 44 and is used to monitor the evaporation rate of boron 46. The second QCM monitor 52 is preferably aimed upward toward the underside of the substrates 14 and is used to monitor leakage of

10   magnesium from the pocket heater 12 through the gap 28.

[0047] Still referring to Fig. 1, a moveable shutter 54 is positioned inside the vacuum chamber 4 between the deposition zone 16 of the pocket heater 12 and the magnesium evaporation cell 34. The shutter 54 is used to prevent the boron 46 from

15   depositing on the underside surface of the substrates 14.

[0048] Fig. 2 shows a perspective view of the underside of the pocket heater 12. As seen in Fig. 2, the deposition zone 16 is in the shape of a pie-shaped wedge. During operation, the shaft 32 rotates the platen 30 containing one or more substrates 14.

20   The substrates 14 repeatedly move between the deposition zone 16 in which boron 46 is deposited and a reaction zone 18 in which pressurized, gaseous magnesium reacts to form MgB_2.

[0049] Fig. 3 is a flow chart illustrating one preferred method of forming MgB_2 on a substrate 14. With reference to Fig. 3, one or

more substrates 14 are loaded onto the platen 30. The platen 30

is then attached to the shaft 32 of the pocket heater 12. A

source of magnesium 38 (preferably in the form of magnesium

pellets) is loaded into the magnesium evaporation cell 34.

5   Boron 46 is then loaded into the electron beam crucible 44. The

lid 6 of the vacuum chamber 4 is then closed and the vacuum

chamber 4 is pumped down to a low pressure (preferably less than

about 10^{-6} Torr).

[0050] Rotation of the platen 30 is then initiated by turning the

10   shaft 32. The platen 30 is rotated at a rate within the range

of about 100 rpm to about 500 rpm. Preferably, the rotation

rate is about 300 rpm. Current is then supplied to heater coils

(not shown) of the pocket heater 12 to heat the substrates 14

contained therein. Current is also supplied to the heater coils

15   42 on the magnesium feed tube 40 that connects the magnesium

evaporation cell 34 and the reaction chamber 26 of the pocket

heater 12. Current is then supplied to the heater coils 36

surrounding the magnesium evaporation cell 34. The typical

temperature of the magnesium evaporation cell 34 needed for

20   deposition is around 650°C.

[0051] Once the temperature of the pocket heater 12, magnesium

evaporation cell 34, and magnesium feed tube 40 have been

established and maintained, the electron beam gun 48 is turned

on and the supplied current is increased until the boron 46

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melts and begins to evaporate. The current supplied to the

electron beam gun 48 is adjusted until the desired deposition

rate is achieved. A typical preferred deposition rate is about

0.1 nm/sec. This can be determined by use of QCM monitor 50.

5   [0052] The shutter 54 disposed between the electron beam crucible

44 and the deposition zone 16 is then opened. Deposition of

boron 46 and film growth of MgB_2 on the underside of the

substrates 14 proceed until the desired thickness of MgB_2 is

reached. Once the desired thickness of MgB_2 is reached, the

10   shutter 54 is closed and the current to the electron beam gun

48, pocket heater 12, magnesium evaporation cell 34, and

magnesium feed tube 40 is reduced to zero (the current to the

magnesium feed tube 40 is left on for a little while in order to

avoid condensation of magnesium and plugging of the feed tube

15   40). The substrates 14 are then removed from the platen 30 once

the substrates have had time to cool down (typically a few

hours).

[0053] In one preferred embodiment of the invention, after the

substrates 14 have had time to cool down, the substrates 14 are

20   turned over to expose the top side of the substrates 14 to the

deposition zone 16 and reaction zone 18. The process described

above is then repeated to deposit a MgB_2 on the second side

(formerly the top side) of the substrates 14. Fig. 4

illustrates the process of depositing MgB_2 on both sides of a

substrate 14.   In this manner, double-sided deposition of MgB_2

can be performed which is required for some applications (e.g.,

microwave filters and microstrip transmission lines).

[0054] The method described herein is particularly advantageous

5   because it is compatible with multilayer deposition of other

materials which is essential for various electronics

applications.   In addition, there is no need to maintain control

of the magnesium/boron flux ratio because the magnesium vapor is

produced independently of the boron deposition process.   The

10   pocket heater 12 used in the process is also beneficial in that

MgB_2 films can be grown on multiple, varied substrates 14

simultaneously.

[0055] The above-described method also effectively avoids MgO

contamination because there are negligible amounts of oxygen and

15   MgO in the reaction chamber 26 where MgB_2 is formed.   In

addition, any magnesium vapor that escapes the reaction chamber

26 should condense, getter, and will not be incorporated into

the grown film.

[0056] Fig. 5 illustrates the resistivity of a MgB_2 film deposited

20   on a polycrystalline alumina substrate.   Fig. 6 illustrates the

resistance of a MgB_2 film deposited on flexible stainless steel

tape.   For both substrates 14, a T_c of approximately 38-39°C is

achieved.

[0057] Fig. 7 illustrates the resistivity of a MgB_2 film deposited on LSAT. Fig. 8 illustrates the resistivity of a MgB_2 film deposited on $LaAlO_3$. Fig. 9 illustrates the resistivity of a MgB_2 film deposited on MgO. Fig. 10 illustrates the resistivity

5 of a MgB_2 film deposited on $SrTiO_3$. Fig. 11 illustrates the resistivity of a MgB_2 film deposited on YSZ. Fig. 12 illustrates the resistivity of a MgB_2 film deposited on r-plane sapphire. Fig. 13 illustrates the resistivity of a MgB_2 film deposited on c-plane sapphire. Fig. 14 illustrates the resistivity of a MgB_2

10 film deposited on m-plane sapphire. Fig. 15 illustrates the resistivity of a MgB_2 film deposited on 4H-SiC. Fig. 16 illustrates the resistivity of a MgB_2 film deposited on Si_3N_4/Si. In this case, a Si_3N_4 buffer layer is first formed on silicon using conventional processes known to those skilled in the art.

15 The Si_3N_4 buffer layer may be formed on the substrate 14 prior to it being loaded into the device 2. Alternatively, the pocket heater 12 may include a nitrogen feed in which the Si_3N_4 buffer layer is formed inside the pocket heater 12.

[0058] Fig. 17 is graph of the estimated surface resistance at 10

20 GHz vs. the inverse reduced temperature (T_c/T) of MgB_2 films deposited on sapphire and alumina substrates. The surface resistance values are estimated because extrinsic losses (R_{res} in Fig. 17) in the measurements had to be estimated and subtracted off in order to arrive at the intrinsic surface resistance R_s of

the MgB_2 film. Samples M1 and M4 of Fig. 17 are MgB_2 films deposited onto a sapphire substrate. Samples M2 and M3 are MgB_2 films deposited onto an alumina substrate.

[0059] In the particular preferred embodiment of the invention, magnesium is heated in an evaporation cell 34 to provide gaseous magnesium to the reaction chamber 26. It should be understood, however, that other elements that are non-gaseous at standard room temperature and pressure may also be used with the present method. In this regard, the particular element (in its non-gaseous state) would be placed into an evaporation cell 34 and heated such that a gaseous form of the element is produced and delivered to the reaction chamber 26.

[0060] For example, TBCCO ($Tl_2Ba_2CaCu_2O_8$ or other phases) may be produced in accordance with the invention. One or more of the non-gaseous elements (i.e., Tl, Ba, Ca, or Cu) may be placed into an evaporation cell 34 which is then connected to the reaction chamber 26 as described above. A separate reaction chamber 26 connected to a source of oxygen is also provided for the oxidation reaction. For example, U.S. Patent No. 6,527,866 illustrates a pocket heater device having a reaction chamber 26 coupled to an oxygen source.

[0061] With respect to TBCCO, one particular method employs placing Tl into the evaporation cell 34 and heating the evaporation cell 34 to form Tl vapor which then passes to a

reaction chamber 26. Another separate reaction chamber 26 containing oxygen is used to oxidize the film. The remaining metals (Ba, Ca, or Cu) are deposited onto the substrate 14 in the deposition zone 16.

5 [0062] Still other superconducting thin films may be formed in accordance with the method described above. These include, for example, bismuth strontium calcium copper oxide (BSCCO), mercury barium calcium copper oxide (HBCCO), and yttrium barium copper oxide (YBCO). Generally, the method described above can be used

10 with any element that has a relatively high vapor pressure at the operating temperature of the pocket heater 12. In addition, the reaction of the gaseous element inside the reaction zone 18 must be self-limiting. That is, using MgB_2 as an example, when magnesium reacts with boron, the reaction does not produce Mg_2B

15 or Mg_3B_2.

[0063] It should also be understood that the present invention may be used to manufacture non-superconducting films. Again, the method described above can be used with any element that has a relatively high vapor pressure at the operating temperature of

20 the pocket heater 12. In addition, the reaction of the gaseous element inside the reaction zone 18 must be self-limiting. Examples of non-superconducting films include, by way of illustration and not limitation, dielectrics, ferroelectrics,

semiconductors such as GaAs, InP, and GaN, magnetic materials,

piezoelectric materials, and the like.

[0064]   Fig. 18 illustrates one alternative embodiment of the

device 2 used to form a thin film on a ribbon of tape 60.   In

5   this embodiment, the pocket heater 12 does not use a rotatable

platen 30 as in the pocket heater 12 shown, for example, in Fig.

1.   Instead, a conveyor arrangement is used to pass the

substrate 14 (in this case a long ribbon of tape 60) through the

pocket heater 12.   In Fig. 18, the pocket heater 12 has four

10   different zones (A, B, C, and D) in which the film forming

process takes place.   As an example, zones B and D might take

the form of deposition zones.   In contrast, zones A and C might

take the form of reaction zones in which a gaseous reactants are

input via feeds 62.   Of course, the particular arrangement shown

15   in Fig. 18 is merely exemplary and other configurations can be

used depending on the type of film produced.

[0065] Fig. 18 illustrates the substrate 14 being unrolled and

rolled on two rotatable drums 64.   In some applications,

however, the nature of the thin film and/or substrate 14 may

20   prevent the ribbon of tape 60 from being stored on drums 64.   In

this case the ribbon of tape 60 is fed and stored in a linear

format.   In addition, while Fig. 18 shows the ribbon of tape 60

making a single pass through the pocket heater 12, the tape 60

may make several passes through the pocket heater 12.   In this

regard, the ribbon of tape 60 may take the form of a single continuous ribbon of tape 60 that wraps around the rotatable drums 64. The continuous ribbon of tape 60 is shown in dashed lines in Fig. 18.

5   [0066] In the case of MgB_2, the deposition of boron onto the tape substrate 14 may occur prior to the tape substrate 14 entering the magnesium pocket (e.g., zones A or C in Fig. 18).

[0067] While the invention is susceptible to various modifications, and alternative forms, specific examples thereof

10 have been shown in the drawings and are herein described in detail. It should be understood, however, that the invention is not to be limited to the particular forms or methods disclosed, but to the contrary, the invention is to cover all modifications, equivalents and alternatives falling within the

15 spirit and scope of the appended claims.